Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A


*Supporting Information*

**From core-shell $MoS_x$/ZnS to open fullerene-like $MoS_2$ nanoparticles.**

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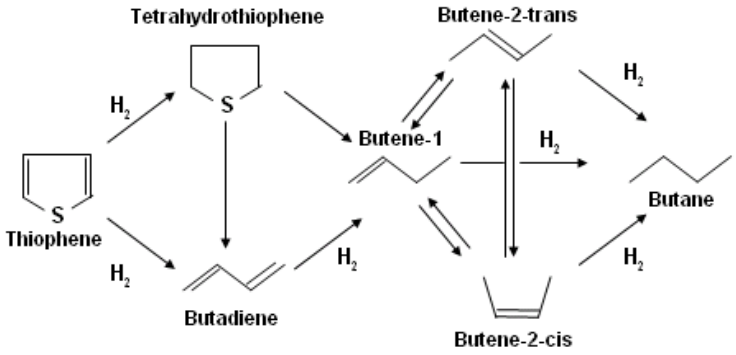



Scheme S1. Thiophene HDS reaction pathways.

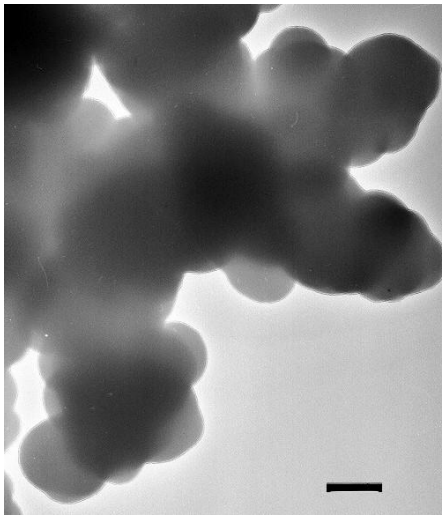
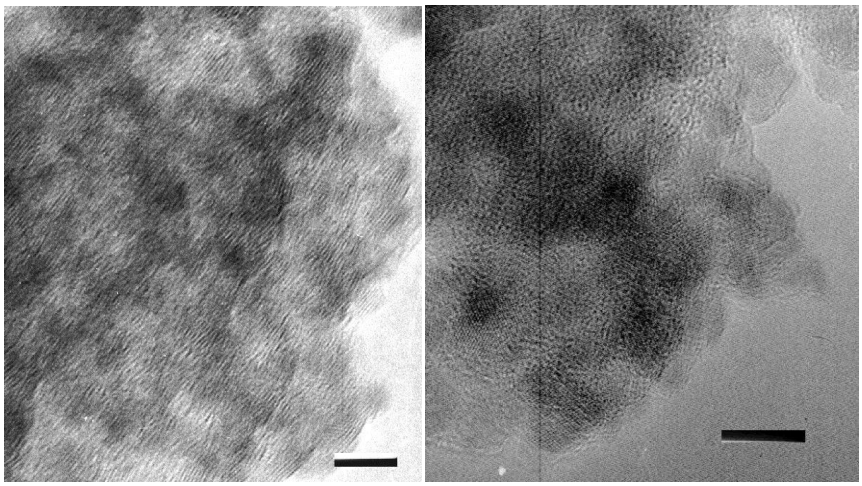


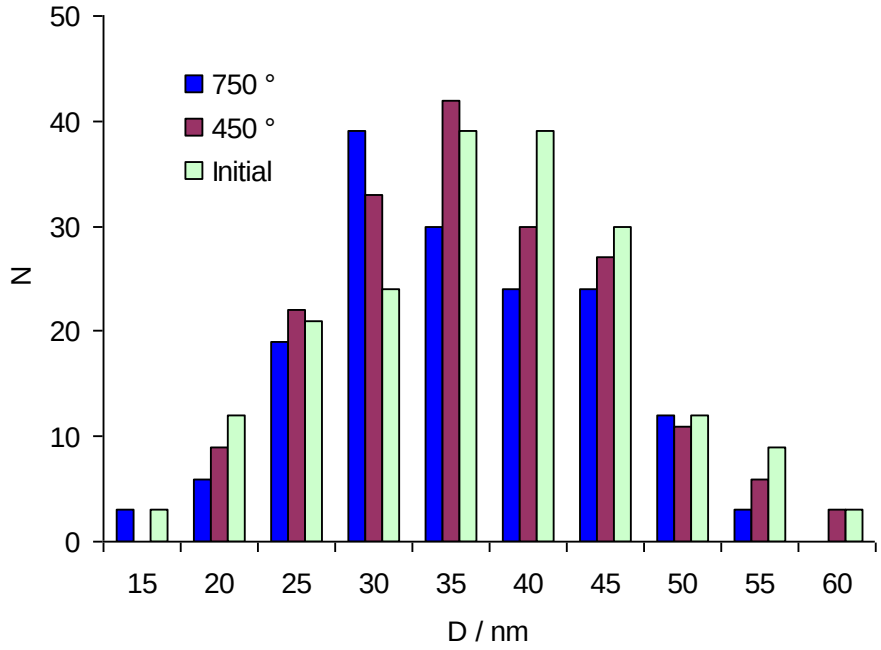
Fig. S1 $MoS_x$ particles obtained in the EG – sulfur mixture without addition of ZnS

Scale bar is 200 nm.

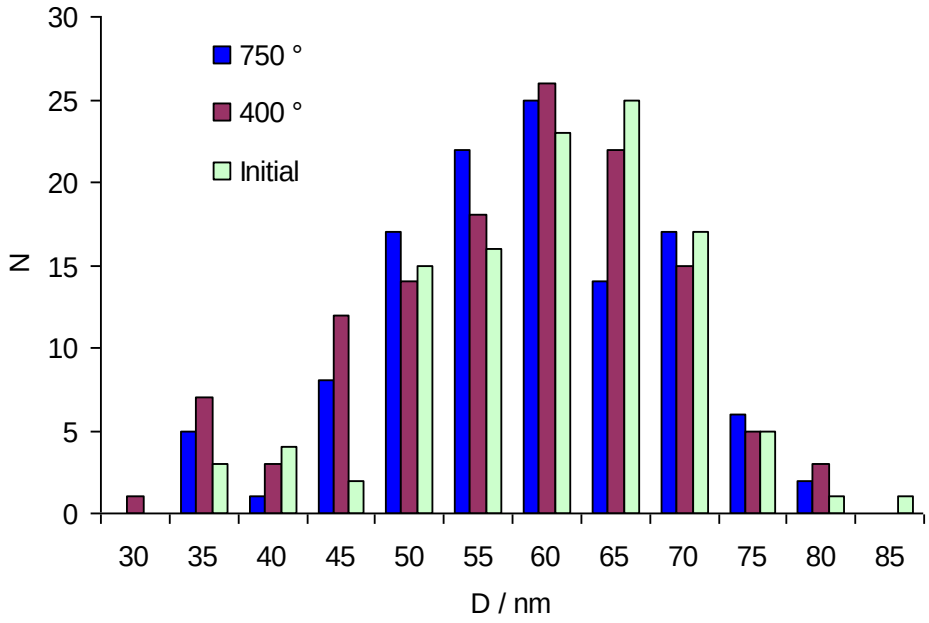


(a) (b)

Fig. S2 TEM image of ZnS seed obtained from the precipitation of $Zn(NO_3)_2$ (a) and $ZnCl_2$ (b) and $Na_2S$ in ethylene glycol. Scale bar is 10 nm for both images. Note that dried powders are analyzed by TEM in which the particles are forcedly agglomerated, whereas in the colloidal suspension they are separated.




a




b

Fig. S3 Histograms of particle size for the sample with Mo/Zn = 1 as a function of thermal treatment: a) Mo/Zn = 1, b) Mo/Zn = 2.

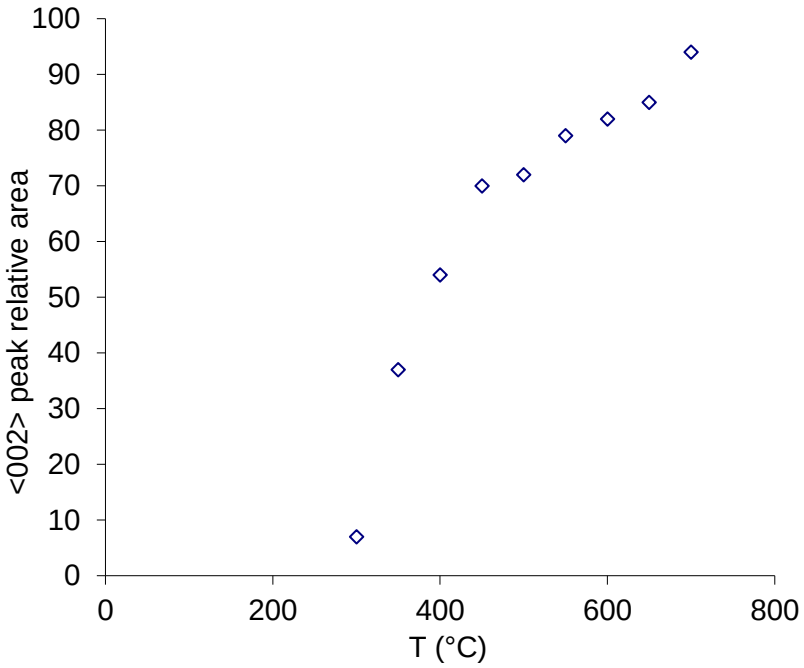



Fig. S4 Relative area of the (002) $MoS_2$ XRD peak as a fucntion of treatment temperature for the Mo/Zn =1 sample. Note the breakpoint above 400 °C corresponding to the completion of $MoS_2$ formation.

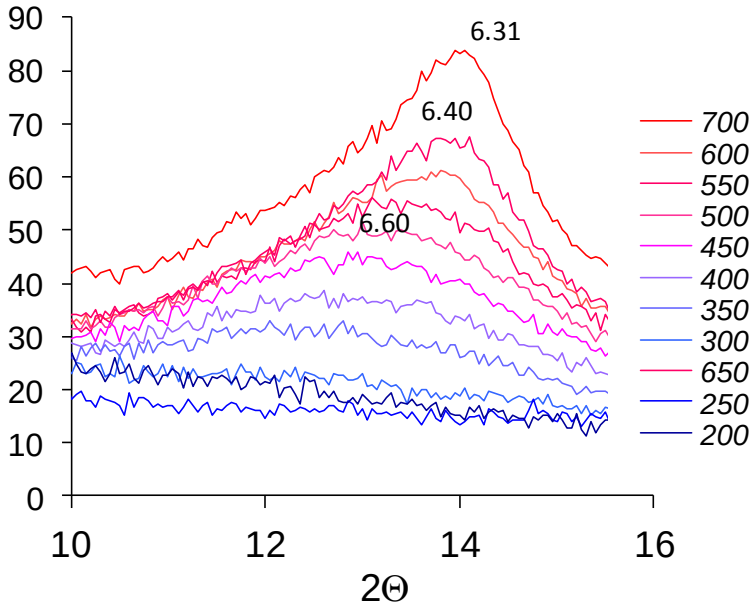



Figure S5 Zoom on the tempreatur evolution of $MoS_2$ (002) diffraction peak

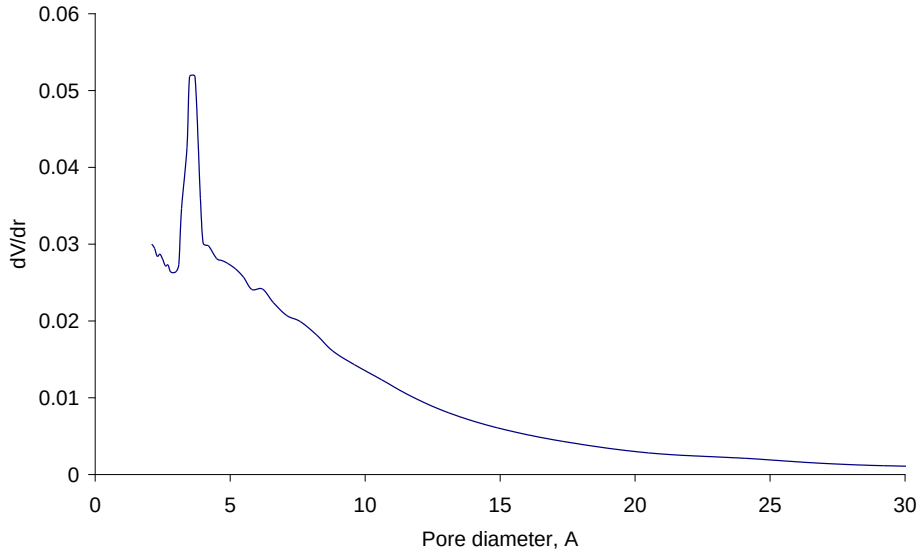



Fig. S6. Pore size distribution in the solid treated under $H_2/H_2S$ mixture at 400°C; Mo/Zn=1. Note the absence oft he characteristic feature corresponding to the mesopores formed by ZnS release.

Table S1 Preparation conditions and some properties of the solids studied in this work.

| Zn precursor | Mo/Zn | Treatment T C° | Treatment gas | Composition[a] | Mo/Zn EDS | Ssp[c] $m^2/g$ | Particle Size, nm |
|---|---|---|---|---|---|---|---|
| Nitrate | 1 | initial | - | $Zn_{0.97}MoS_{4.80}$ | 2.9 | -[d] | 36 |
| Nitrate | 1 | 400 | $H_2/H_2S$ | $Zn_{0.97}MoS_{3.11}$ | 2.8 | 33 | 29 |
| Nitrate | 1 | 500 | $H_2/H_2S$ | $Zn_{0.97}MoS_{3.13}$ | 2.8 | 31 | 31 |
| Nitrate | 1 | 600 | $H_2/H_2S$ | $Zn_{0.97}MoS_{3.07}$ | 3.8 | 40 | 28 |
| Nitrate | 1 | 750 | $H_2/H_2S$ | $Zn_{0.97}MoS_{3.03}$ | >50[b] | 59 | 28 |
| Nitrate | 1 | 750 | $H_2$ | $Zn_{0.97}MoS_{2.78}$ | >50 | 58 | 29 |
| Nitrate | 1 | 750 | $N_2$ | $Zn_{0.97}MoS_{3.08}$ | >100 | Nd | 27 |
| Nitrate | 2 | initial | - | $Zn_{0.44}MoS_{3.9}$ | 4.5 | - | 60 |
| Nitrate | 2 | 400 | $H_2/H_2S$ | $Zn_{0.44}MoS_{2.55}$ | 4.2 | 25 | 47 |
| Nitrate | 2 | 750 | $H_2/H_2S$ | $Zn_{0.44}MoS_{2.46}$ | >50 | 41 | 44 |
| Nitrate | 2 | 750 | $N_2$ | $Zn_{0.44}MoS_{2.67}$ | >100 | 38 | 46 |
| Chloride | 1 | initial | - | $Zn_{0.94}MoS_{4.60}$ | 3.2 | - | 39 |
| Chloride | 1 | 400 | $H_2/H_2S$ | $Zn_{0.94}MoS_{3.12}$ | 2.9 | 30 | 33 |
| Chloride | 1 | 750 | $H_2/H_2S$ | $Zn_{0.94}MoS_{3.01}$ | >50 | 57 | 29 |
| Chloride | 1 | 750 | $N_2$ | $Zn_{0.94}MoS_{3.00}$ | >100 | 58 | 31 |
| Chloride | 2 | initial | - | $Zn_{0.48}MoS_{4.1}$ | 4.8 | - | 57 |
| Chloride | 2 | 400 | $H_2/H_2S$ | $Zn_{0.48}MoS_{2.59}$ | 4.5 | 30 | 48 |
| Chloride | 2 | 750 | $H_2/H_2S$ | $Zn_{0.48}MoS_{2.46}$ | >100 | 47 | 46 |

[a] – elemental analysis; [b] – in the $MoS_2$-containing part only; c – BET specific surface area; d – BET surface area of the initial samples can not be determined since they slowly decompose under outgasing conditions.